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PROCESS FOR MONITORING AND CONTROLLING NITRATING PROCESSES WITH THE AID OF AN ONLINE SPECTROMETER

BACKGROUND OF THE INVENTION

The present invention relates to a process for monitoring and for controlling a nitrating process, in particular for the nitration of toluene, with the aid of a computer-assisted, matrix-specific calibration model and a process model.

Various nitration processes are known in the prior art. For example, toluene is nitrated with nitric acid to yield nitrotoluidines by way of intermediate dye products. It is also known to nitrate toluene with mixed acids to yield nitrotoluene and dinitrotoluene. Dinitrotoluene is, for example, processed further to yield diamines, diisocyanates, trinitrotoluene or phloroglucinol.

For economic reasons, the aim in the course of nitration is to conduct the nitration with as small an excess of acid as possible. To this end, it is known from the state of the art to take samples from the process manually and to examine them analytically in the laboratory. The process is then readjusted manually when required.

One disadvantage of such manual sampling and adjustment is the high cost of labor for the sampling and for the laboratory analysis. Another disadvantage is that the effort increases linearly with the number of measuring-points. Furthermore, manual sampling is problematic from the point of view of industrial safety, since, particularly in the case of 2-nitrotoluene, it is a question of working with a substance that is detrimental to health. Therefore in the course of handling 2-nitrotoluene, the wearing of respiratory protection at all times as a precaution is prescribed.

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Another disadvantage of manual sampling with subsequent laboratory analysis is the fact that readjustment of the process can only be effected irregularly and after relatively long time-intervals. This may result in use of a relatively large excess of acid; the plant cannot then be operated in optimal manner, either technically or economically.

SUMMARY OF THE INVENTION

An object of the present invention is therefore to create an improved process for monitoring and controlling nitrating processes that enables a diminution of the excess of acid. Further objects underlying the invention are to create an online method of measurement with a computer-assisted process model and to create an appropriate production process for the nitration.

The objects of the present invention are achieved by online spectrometric measurement of the acid phase from the reaction mixture and transmission of that data to a process control system.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a flow chart for the process of the present invention for improved monitoring and control of nitrating processes by virtue of the online measurement of the acid phase and the improved metering of nitric acid.

Figure 2 is a block diagram of a two-stage nitration process according to the invention.

Figure 3 shows various NIR spectra for various concentrations of nitric acid.

Figure 4 is a flow chart for the process of creating the matrix-specific calibration model, the validation and enhancement thereof.

Figure 5 is a schematic representation of a bypass with a measuring cell.

DETAILED DESCRIPTION OF THE INVENTION

In accordance with the present invention, the acid phase recovered from the nitration reaction mixture is spectrometrically examined online. This is preferably done by infrared spectrometry. Such measurements are also designated as infrared spectroscopy. Appropriate IR spectrometers, in particular for the near-infrared range (NIR) are commercially available, for example from Polytec GmbH and other manufacturers.

In a preferred embodiment of the invention, the content of nitric acid in the acid phase is determined online after nitration by means of an NIR spectrometer and a suitable computer-assisted calibration model. Data for quantifying the content of nitric acid are then transmitted from the NIR spectrometer to the process control system, for example via a field bus. On the basis of the nitric-acid content in the acid phase that is determined after nitration, regulation by the process control system for the supply of nitric acid is possible. The online control of a production plant for the purpose of regulating various polymerization parameters is disclosed in US 5,121,337 and EP-0 948 761 B1 [*sic*]. In these disclosed processes, a predictive model created on the basis of measured spectra is used.

In a particularly preferred embodiment of the invention, the measured NIR spectrum is evaluated with the aid of a matrix-specific calibration model. The physical matrix is predetermined by the nitrating process and is dependent on the parameters of the process. With the aid of chemometric methods, the measured spectra are referenced against results obtained from laboratory examinations.

This is effected in such a way that the same sample for which an NIR spectrum was determined online is also analyzed in the laboratory with the aid of titration measurements. By virtue of the examination and the comparison of a suitable

number of varying samples, it is possible to create a matrix-specific calibration model with the aid of chemometry. This matrix-specific calibration model is stored on a computer that is programmed to control the recording of the spectrum and to evaluate the measured spectrum online with the aid of the calibration model, so that the nitric acid content is available to the process control system online.

The nitration of toluene to yield dinitrotoluene (DNT) is generally conducted in two stages. The spectrometric examination of the acid phase is undertaken at least after the second nitrating stage, in order to readjust the supply of nitric acid to the first and/or the second nitrating stage.

In another preferred embodiment of the invention, the NIR spectrometer is connected to several measuring-points. The NIR spectrometer is multiplexed, in order to carry out spectrometric measurements in succession at the various measuring-points. By reason of this multiplex operation of the NIR spectrometer, the measurement effort increases degressively with the number of measuring-points.

The invention is particularly advantageous because it enables distinctly improved process control. In particular, the invention enables the production plant to be operated continuously, close to the technical and economic optimum. Another advantage is the improvement in industrial safety.

Preferred embodiments of the invention will be elucidated in greater detail below with reference to the drawings.

Figure 1 is a flow chart for a process according to the invention for monitoring and controlling nitrating processes. In step **100**, nitric acid (HNO_3) is supplied continuously to a nitrating stage. The product of the nitrating stage is a two-phase

system composed of nitrated organic phase and acid phase. An NIR spectrum of the acid phase is recorded by means of a suitable measuring cell and an NIR spectrometer. This is undertaken in step **102**. In step **104**, the HNO_3 content in the acid phase is determined by evaluation of the NIR spectrum by means of a matrix-specific calibration model. This measurement is preferably undertaken inline or online, i.e. in the current product stream.

In step **106**, the HNO_3 content that has been ascertained is transmitted to a process control system. In step **108**, the quantity of continuously supplied HNO_3 is readjusted manually or by the process control system, in order to reduce the HNO_3 content in the acid phase if necessary.

Figure 2 is a block diagram of an embodiment of an appropriate plant. The plant has a reactor **200** for the purpose of realizing a first nitrating stage (mononitration MNT). The feed materials are toluene **201**, sulfuric acid **202** and nitric acid **203**. The product of the first nitrating stage is a two-phase system which is separated, in the separator **208** connected downstream, into the organic phase **211** and the acid phase **209**.

A measuring-point **205** for recording an NIR spectrum of the acid phase may be provided downstream of the reactor **200**. To this end, an NIR spectrometer **220** may be connected to the measuring-point **205** via an optical waveguide **206**.

The separator **208** is followed by a further reactor **210** for the purpose of realizing the second nitrating stage (dinitration DNT). The feed materials are MNT **211**, sulfuric acid **212** and nitric acid **213**. The product of the second nitrating stage is a two-phase system which is separated, in the separator **218** connected downstream, into the organic phase **230** and the acid phase **219**.

A measuring-point **215** is preferably arranged downstream of the output of the reactor **210**. The NIR spectrometer **220** is connected to the measuring-point **215** via an optical waveguide **216**. As a result, NIR spectra for the acid phase can be recorded.

The measuring-points **205** and **215** may each be operated with their own spectrometer; however, they are preferably operated with a single spectrometer **220** which switches between the measuring-points **205** and **215**.

The NIR spectrometer **220** passes on the measured NR spectra for evaluation by means of the matrix-specific computer-assisted calibration model **222**. The computer with the matrix-specific calibration model **222** passes on its results for the content of nitric acid to the process control system **224**. The subsequent regulation (manual or automated) of the metering **207** or **217** of the first **200** and/or the second **210** nitrating stage, respectively, permits improved monitoring of the process and improved process control for the content of HNO_3 in the acid phase within the range 0-5 %, in particular close to 0 %, preferably within the range from 0 % to 0.3 %.

In a preferred embodiment of the invention, the HNO_3 content is determined only at measuring-point **215** and not at measuring-point **205**. The measurement of the HNO_3 content at measuring-point **215** after the second nitrating stage is generally sufficient for regulation of the production of dinitrotoluene.

In the case where production of dinitrotoluene is undertaken in multiple lines, several parallel measuring-points **215** may be provided. All the measuring-points **215** are then preferably connected to the same NIR spectrometer **220**, which operates in multiplex mode. The NIR spectrometer **220** accordingly measures the spectra at the measuring-points **215** in succession, in cyclic sequence. By virtue of the multiplexing of the NIR spectrometer **220**, it is possible for the

instrumentation effort for implementation of the HNO_3 measurements to be optimized.

Figure 3 shows the spectra **300, 302** and **304**. Spectrum **300** has been recorded for 75 % sulfuric acid without nitric-acid content. Spectrum **302** has been recorded for 75 % sulfuric acid with 1 % nitric-acid content. Spectrum **304** has been recorded for 75 % sulfuric acid with 5 % nitric-acid content.

The measured NIR spectra **300, 302** and **304** accordingly differ distinctly, depending on the percentage content of nitric acid in the acid phase. In corresponding manner it is possible for the nitric-acid content in the acid phase to be determined by measurement of the NIR spectrum. To this end, a matrix-specific calibration model based on comparative titration measurements is preferably used.

Figure 4 illustrates the procedure for obtaining a database for the generation of a matrix-specific calibration model. Step **400** illustrates the creation of such a calibration model; step **420** illustrates the validation of this model.

Step **402** represents the physical matrix, which is process-specific and dependent on the process parameters with regard to its special composition.

The nitric-acid content, which is ascertained by means of manual sampling **406** with subsequent titration **408**, is used for creation of the calibration model. Sampling and titration may also be undertaken in automated manner and online, or manually and offline. In parallel, a measuring cell, with which the NIR spectra pertaining to the samples can be recorded, is installed in the process flow. This is undertaken in step **404**.

In step **410,** the results from the titration determinations are compared and are correlated with the respective NIR spectra with the aid of chemometric methods.

In step **412,** all of the comparisons between all of the NIR spectra and all of the titration results are combined and are correlated in a model. The parameters of the model are adapted and adjusted in such a way that the content of nitric acid for the existing substance system and the existing process parameters are reproduced optimally. Once the model has been adapted and optimized, the matrix-specific calibration model is available at the end of step **412**.

Subsequently, in step **420**, validation of the model is undertaken in respect of the current process. Whenever titration results are available in a manner temporally appropriate to the spectra arising from the process, said results can be integrated in accordance with step **400** for the purpose of successive enhancement of the model (step **422**).

Figure 5 shows an embodiment of the invention with a measuring-point (for example, measuring-point **215** of Figure 2). The product stream of the current production flows through the line **500**. A bypass **502** is located on the line **500**. The bypass **502** has a measuring cell **504**. Located upstream and downstream of the measuring cell **504** in the direction of flow is a shut-off device **506** and **508**, respectively. The shut-off devices enable access to the measuring cell while the product stream is running.

List of Reference Symbols

reactor	200
toluene	201
sulfuric acid	202
nitric acid	203
measuring-point	205
optical waveguide	206
regulation of metering	207
separator	208
acid phase	209
reactor	210
mononitrotoluene (MNT)	211
sulfuric acid	212
nitric acid	213
measuring-point	215
optical waveguide	216
regulation of metering	217
separator	218
acid phase	219
NIR spectrometer	220
calibration model	222
process control system	224
organic phase	230
spectrum	300
spectrum	302
spectrum	304
line	500
bypass	502
measuring cell	504
shut-off device	506
shut-off device	508

Although the invention has been described in detail in the foregoing for the purpose of illustration, it is to be understood that such detail is solely for that purpose and that variations can be made therein by those skilled in the art without departing from the spirit and scope of the invention except as it may be limited by the claims.